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# Alternate Sources for Propellant Ingredients

Naval Surface Weapons Center White Oak Lab Silver Spring Md



**ALTERNATE SOURCES FOR PROPELLANT INGREDIENTS** 

BY M.E. Houser M.I. Fauth

7 JULY 1976

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NAVAL SURFACE WEAPONS CENTER WHITE OAK LABORATORY SILVER SPRING, MARYLAND 20910

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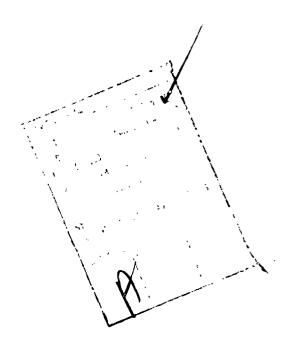
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ALTERNATE SOURCES FOR PROPELLANT INGREDIENTS: FINAL REPORT FOR THE FISCAL
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#### ABSTRACT

a survey has been made to evaluate the criteria which determine whether the supply status of a substance required for the production of propellants and related Navy materials is critical, and for which materials alternate sources are required or should be developed. Lists of materials are presented for the following categories: (1) not commercially available and presently manufactured or processed at the Naval Ordnance Station, Indian Head; (2) commercially available but supply problems exist for a variety of reasons; (3) sole source; (4) medical/OSHA/EPA problems; (5) dependent on foreign imports; and (6) specification problems.

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Propellants Chemistry Branch

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NAVAL SURFACE WEAPONS CENTER

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- Availability of domestic reserves (Table I)
- 2. Availability of substitutes
- 3. Number and location of foreign suppliers (Table II, III)
- 4. Ideology of foreign suppliers
- 5. U. S. stockpile objectives
- 6. Number of producers
- 7. Present and future production capacity
- 8. Regulatory constraints
- 9. Energy consumption (Table IV)
- 10. DoD usage as percent of total

#### Based on these factors, the most critical 21 materials were:

1.	Aluminum	12.	Niobium (Columbium)
2.	Chromium	13.	Tin
3.	Manganese	14.	Tungsten (Wolfram)
4.	Titanium	15.	Antimony
5.	Arsenic	16.	Tantalum
6.	Beryllium	17.	Mercury
7.	Cobalt	18.	Lead
8.	Nickel	19.	Silver
9.	Platinum group	20.	Zinc
10.	Asbestos	21.	Mica
11.			

Present and prospective materials shortages may be due to one or more of the following categories:

- 1. Geologic dependent on crustal abundance of the element or ore;
- 2. Geographic whether supplies in the U. S. or friendly nations are inadequate;
- 3. Dependency (a) the substance is a by-product and production of the major product is curtailed; (b) there is substitution of a material that is in short supply;
- 4. Environmental constraints regulations of OSHA or EPA affect production or use of the product;
- 5. Plant capacity when demand increases faster than predictions;
- 6. Supply-Demand perturbations these are temporary imbalances in the supply-demand cycle.

A number of lists of critical materials have been proposed based on various criteria. For comparison purposes, several of these lists are appended.

#### a. Scarcity of U. S. and World Reserves

1.	Mica sheet	5.	Mercury	9.	Asbestos
2.	Silver	5.	Graphite	10.	Tantalum
3.	Bismuth	7.	Tin	11.	Tungsten
4.	Fluorspar	8.	Zinc	12.	Cadmium

### b. <u>Scarcity of U. S. Reserves and Politico-economic Problems</u> <u>Affecting World Trade</u>

1.	Petroleum and Natural Products	8.	Niobium
2.	Chromium	9.	Antimony
3.	Manganese	10.	Cobalt
4.	Titanium (Rutile)	11.	Thorium
5.	Nickel	12.	Platinum
6.	Palladium	13.	<b>Yanadium</b>
7.	Aluminum (Bauxite)	14.	Copper

#### c. Stanford Research Institute List of Critical Materials

	Material	Percent DOD Use
1. 2. 3.	Mercury Mica sheet	9 8
4.	Manganese Platinum group Fluorine	6 4
6. 7.	Graphite Tungsten	- - 7
8. 9.	Chromium Antimony Cobalt	6 7 13
11.	Nickel Asbestos	- 4
13. 14.	Yin Aluminum	7 -

#### d. U. S. Army War College Vulnerability Index

Material	Vulnerability Index
Chromium	34
Platinum group	32
Tungsten	27
Manganese	23
Aluminum	22
Titanium	20
Cobalt	20
Tantalum	16
Nickel	14
Mercury	11
Tin	6

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#### OBJECTIVES

The objectives of this program are to identify critical supply areas for materials necessary for the preparation of propellants and explosives used or manufactured by the Navy, to generate or acquire alternative or back-up sources for critical ingredients, and to develop substitute materials and technology for their utilization.

#### BACKGROUND

The problems associated with procurement of military supplies are well known and have been widely discussed. These difficulties are especially acute during wartime, when materials are most limited and usage by the armed forces is at a maximum. During times of crises and shortages, technological advancement is stimulated to an inordinate degree and substitutes for military and civil use are adopted. This effect was illustrated by the 'ersatz' economy of Germany during the World Wars and by the rapid adoption of synthetic rubber in the United States in 1942 to 1945. It is a serious mistake, however, to assume that development can be deferred until the necessity occurs. Basic knowledge and applied development with emphasis on processing capability in existing facilities must be available before the fact of the emergency.

The United States is not presently engaged in an active conflict and hopefully will not be in the foreseeable future. This, then, is the ideal period for advanced planning and development of alternative sources and substitute materials. Four situations which are unique in this country during peacetime are acting to force the issue. The nationwide shortage of petroleum and petro-chemicals is limiting availability of many materials commonly used by the propellant and explosives industry. The parallel energy shortage may be expected to affect production of ingredients such as metal fuels and oxidizers that require large expenditures of electricity for preparation. The least effect of the petroleum shortage would be a drastic increase in the cost of many materials; the greatest consequence would be severe curtailment or disappearance of other supplies; either of these will impair advance planning and development.

The second significant factor with impact on military logistics is pollution control and abatement measures. The increasing awareness of the necessity for protecting the environment, workers, and the general public from unacceptable hazards presented by noxious, toxic, corrosive or carcinogenic materials which lead to the regulations of OSMA, EPA, and those enacted by the States such as California, are having a major impact on the propellant and explosives industry. While the use of any process may not be prohibited outright, the degree of protection required will increase costs and reduce or eliminate the profit margin.

The third factor affecting supplies is the movement of manufacturing operations out of the country. There are a number of reasons for this trend. Producers obtain cheap labor, tax advantages, favorable import/export duty positions, and some freedom from restrictive decrees. The last reason is related to some extent to current pollution abatement measures. No matter how seemingly logical or valid the rationale, the impact on propellants is serious. It is increasingly more difficult to find domestic suppliers. Dependency on foreign sources of minerals and ores should also be noted and minimized. The fallacy of incurring dependency on foreign sources is obvious and requires no comment here.

The fourth factor impacting on military supplies is the new technology and advancement of the state-of-the-art. As new techniques, processes, or materials are developed, old ones are reduced or abandoned. In many cases, the Navy is locked into a specified propellant or system and is unwilling or unable to change because of specifications or requalification problems.

The Naval Surface Weapons Center and The Naval Ordnance Station, Indian Head, working as an integrated team, have considerable experience in and facilities for preparation of propellants, explosives, intermediates and ingredients. Chemicals manufactured or processed at NAVORDSTA, Indian Head, include nitroguanidine, nitro-plasticizers, MAPO, nitroform, hydrazine nitroform, hydroxylamine perchlorate and hydroxylamine nitrate, and many others. Currently, the manufacture of UDMH (unsymmetrical dimethylhydrazine) at NAVORDSTA, Indian Head, is in progress. The success of these projects suggested that the program of 'Alternate Sources for Propellant Ingredients' could be pursued to good advantage. The operation at a government operated facility insured no conflict of interest or advantage to proprietary interests.

#### APPROACH

A list of materials used or necessary in the manufacture of propellants and explosives was prepared. Domestic sources were indicated and the degree of criticality assessed. Alternative commercial sources for equivalent supplies were sought. Where necessary, plans for preparing ingredients in-house were formulated. In extreme cases, laboratory scale-up and investigations have already begun on materials needed immediately and unavailable commercially. Interviews with ehemists and engineers at NAVORDSTA, Indian Head, literature research, meetings, etc., were all used to gather the data for the list of materials and the reasons for their scarcity or criticality.

#### GENERAL DISCUSSION

A vulnerability index has been proposed to rank essential materials in a relative order of criticality. This index involves an evaluation of the following ten factors:

Relief measures when the supply of essential foreign material is interrupted or made unreasonably expensive are:

- Develop available low-grade domestic resources;
- 2. Use intensive research to find new deposits;
- 3. Use substitutes for some applications;
- 4. Develop new or different technology to replace functions or use of scarce material;
- Use conservation to decrease amount used and extend life of products using the material;
- 6. Minimize dissipative uses;
- 7. Encourage efficiency during processing;
- 8. Recover and recycle;
- 9. Stockpile until above steps can be put into operation.

#### A conservation technology of materials should include:

- Development and application of improved techniques of mineral extraction;
- 2. Economy of materials in efficient application of the best available technology in design processing and shaping of material;
- 3. Dollar economy-utilization of scrap, reduction of transportation costs;
- 4. Develop alternate materials, e.g., metal composites instead of metals;
- Develop improved uses for abundant materials such as silicon, and silicon dioxide;
- 6. Flexibility of use;
- 7. Development of effective equipment;
- 8. Reliability improvement:
- 9. Enhance properties of materials;
- 10. Be watchful of impact of new technology on materials requirements.

It is evident from the above that certain materials appear on several lists and that almost all of the work done to date has involved metals and minerals. This distorts the picture, since such categories as fuels and energy sources, petro-chemicals and plastics, foods and fibers, and manufactured goods are not included.

Considerable savings of critical materials could be achieved by recycling. The amount of material recycled varies greatly, as indicated by the following list:

#### Old Scrap Recycled in U. S. in 1972

Material	Percent of U. S. Consumption
Iron	37
Lead	37
Copper	20
Aluminum	6
7inc	5

Material	Percent of U.S. Consumption
Chromium	15
Nickel	35
Tin	17
Antimony	60
Magnesium	3
Mercury	26
Tungsten	4
Tantalum	12
Cobalt	1
Selenium	3
Silver	23
Gold	28
Platinum group	21

Recycling could provide about 40 percent of the material requirements for manufacturing (metals, glass, plastics, fibers, rubber) but less than 5 percent of the U. S. yearly total materials requirement can be met from post-user scrap.

The advantages of recycling are:

- 1. It relieves pressure on primary materials resource base;
- It reduces dependence on foreign imports;
- 3. It reduces energy requirements for processing;
- 4. It reduces environmental pollution.

Areas of major recycling efforts needed are:

- 1. Extraction of materials and energy from urban refuse;
- 2. Upgrading and utilization of junk-car and related scrap;
- Utilization and/or stabilization of mine, mill and mineral processing wastes;
- 4. Recovery of materials from industrial waste.

Conservation of materials in design processes should include:

- Favoring abundant over scarce materials;
- 2. Favoring renewable and recyclable materials;
- 3. Efficient design-use of materials.

Reduction of material processing waste can be effected by:

- Reduced machining, cutting, grinding;
- Using preforms, e.g., forgings and castings;
- 3. Using deformation and additive-powder metallurgy extrusions;
- Using friction welding, adhesive bonding, non-destructive test methods for reduction of critical materials needed.

Miscellaneous products where imports exceed 50 percent of U.S. consumption include:

- 1. Natural rubber
- 2. Castor oil
- 3. Cordage fiber
- 4. Shellac
- 5. Vegetable tannin

A survey of the availability of chemicals in 1974 gave the following information:

1. Fifteen of twenty-five respondents reported problems;

2. Plastics users reported problems of price instability, availability, OSHA-EPA requirements, toxicity;

 Petrochemicals users reported problems of feed-stock availability and long lead times;

4. Fuels and lubricants users experienced allocation problems, crude oil shortages and excessive prices;

5. Specific compounds which were problems were: gasoline, fuel oil, Petrolube, alcohols, toluene, methylethyl ketone, resins bonding agents, fiberglass, caustic soda, cellosolve acetate, trichloroethane, phenol, furfuryl alcohol, Epons/epoxides, silicones, chlorinated solvents, phenolics, potting compounds, ablative coating, fluorosilicone, Lexan, strontium chromate, paints.

#### SPECIFIC MATERIALS:

The materials, metals/ores and chemicals were separated into six main categories:

- 1. Materials not available commercially, and being manufactured/processed at NAVORDSTA, Indian Head;
- 2. Materials available commercially but in critical supply status for specific reasons stated;

3. Materials available commercially from sole source only;

4. Materials in a critical status because of medical/EPA/OSHA reasons;

5. Materials dependent on foreign importation;

6. Materials with specification problems.

Each material was placed in one of the above categories considered most critical to that material; many could appear on more than one list. A second designation was added to each write-up to indicate secondarily whether the material is critical from the standpoint of:

- (S) sole source
- (0) derived from the oil/petroleum industry

(E) is energy intensive

(P) is a pollution/health problem (OSHA/EPA)

(L) has low DoD usage

- (F) is dependent on foreign importation
- (K) has trouble meeting specifications

An individual listing of all these materials and discussion follows:

#### Category 1:

Materials not available commercially, and being manufactured/processed or planned to be manufactured at NAVORDSTA, Indian Head:

Unsymmetrical dimethylhydrazine, hydrazine 2,4-Dinitrophenoxyethanol and 2,4-Toluenediamine MAPO
Nitroguanidine
Nitrocellulose
Triaminotrinitrobenzene and sym-trichlorobenzene
Bis-(2,2-Dinitropropyl)-Acetal
Bis-(2,2-Dinitropropyl)-Formal

#### Category 2:

Materials available commercially but in critical status for specific reasons stated:

Caustic soda and soda ash Aluminum powder Perchlorate salts, ammonium and potassium Carbon black Graphite

#### Category 3:

Materials available commercially from sole source only:

Viton-A
Resins and plasticizers
Butarez, Types I and II
PDX
HMX
2-Nitrodiphenylamine
Desensitizing wax
Milori blue

#### Category 4:

Materials in a critical status because of medical/EPA/OSHA reasons:

Lead salts (10 different items)
Trichloroethylene
2,4-Toluene diisocyanate
Pentachlorophenol
Phenyl beta-naphthylamine
Shelldyne-H
Kevlar

#### Category 5:

Materials dependent on foreign importation:

Barium chromate, ammonium dichromate and chromium Manganese powder and manganese delay composition Titanium and titanium dioxide Tungsten Glyceryl mono-and tri-ricinoleates (castor oil) Cobalt naphthenate Shellac Elba solvent Nitroform Ammonium oxalate Sodium barbiturate

#### Category 6:

Materials with specification problems:

Zirconium, zirconium-nickel alloy and zirconium oxide Ferric oxide

#### <u>Category 1:</u>

by Marazine: Category 1, S, P. Unsymmetrical dimethyl-hydrazine (1,1-dimethylhydrazine) is used as a fuel in the Air Force Titan 2 ICBM, and in NASA's Titan 3 and Agena launch vehicles. OSHA regulations against the use of nitrosoamines, one of which was used by FMC Corporation in the manufacture of UDMH, caused a shortage of UDMH during 1974 and 1975. In early 1976, FMC closed its Baltimore, Maryland plant permanently after completing its Air Force contract. NAVORDSTA, Indian Head is currently manufacturing UDMH, using a different starting compound than the N-nitroso-dimethylamine used by FMC. UDMH is used today almost solely for the launching of military and civilian satellites and spacecraft. The current U. S. market for the fuel is estimated to be two million pounds annually. Commercial suppliers were reluctant to get into UDMH production because of the limited market and the necessity for developing a non-hazardous and non-polluting production process.

Hydra. ne, also used as a rocket fuel, is currently being worked on at NAVORDSTA, Indian Head, where a process for distillation of the technical grade material to produce military specification (98%) fuel is being scaled-up.

There may be future OSHA-EPA problems with both of these compounds. UDMH is toxic and has induced tumors in mice but not in rats. In exposed persons handling rocket fuels containing UDMH, local irritation of membranes,

central nervous system effects, and possible liver damage were noted. Threshold limit values are 0.5 parts per million (ppm) for UDMH and 1 ppm for hydrazine. Because of its acute toxic nature leading to liver and red blood cell damage, human exposure to hydrazine should be avoided.

- 2.4-Dinitrophenoxyethanol: Category 1, S. P. L.This compound is used in the Mark 6 gas generator. It contains 20 to 30 percent of 1,2-di(2,4-dinitrophenoxy)ethane. There is no source of this material and the total requirement is being made by NSWC at NAVORDSTA/IH using 2,4-dinitrochlorobenzene as the starting material. The starting compound is a primary skin irritant and is extremely toxic by ingestion or inhalation. Supply problems are probably due to toxicity and lack of a commercial market.
- 2,4-Toluenediamine: Category 1, S. F. P. L. This compound, used in the Mark 6 gas generator, has no domestic source and no source at all for the pure material. A technical grade material, 86% purity, is being imported from West Germany and this is purified by NSWC at the NAVORDSTA/Indian Head. This compound has a marked toxic effect on the liver and is a skin irritant. Supply problems probably involve the following: lack of a commercial requirement for pure material; DoD consumption is small, and toxicity problems with the compound.

MAPO: Category 1, P, K. Tris(2-methyl-1-aziridinyl) phosphine oxide (MAPO) is used as a crosslinking agent for polymers containing active hydrogen sites in the following programs: Sidewinder MK 9, 12, 17, 18 Catapults; MK 56 Standard Missile. The commercial material contains a minimum of 92% MAPO as determined by a reactive imine assay and no more than 0.5% volatile material. The Navy requirement is for a minimum imine content of 96 percent. Currently there are two suppliers but neither meets the purity requirements, so that further purification at NAVORDSTA/IH is needed after the material is received. MAPO is highly toxic by skin absorption and ingestion. It has been reported to have induced leukemia in rats but the data are insufficient for evaluation of its carcinogenicity.

Nitroguanidine: Category 1, E, S. During the middle 1950's, the Naval Ordnance Station, Indian Head, was preparing large quantities of nitroguanidine by the Roberts Process. More recently, a Canadian Company was the sole source; this company has discontinued production, so there is presently no source of supply except the stockpile. The NAVORDSTA/IH produces high bulk nitroguanidine (HBNQ) from nitroguanidine drawn from the Crane, Indiana stockpile. This material is used in the Tartar, MK 56 Standard Missile, and Improved Shrike programs.

Nitrocellulose: Category 1, S, L, K. In the past, all nitrocellulose (NC) used in manufacturing double-base propellants at the NAVORDSTA/Indian was manufactured by a batch process. Radford Army Ammunition Plant has discontinued manufacture of batch-nitrated NC. The new NC obtained will

be from a continuous process which produces material with different physical properties. Use of this material will require evaluation and may present problems in some applications because of the different physical properties.

This is an example of a supply problem resulting from technological change and lack of a large market. Some time ago, the DuPont Company phased out its production of NC and similar materials.

The NAVORDSTA/Indian Head also uses NC for producing Plastisol Nitrocellulose (PNC) used in Trident, Poseidon, Zuni, etc.

1,3,5-Triamino-2,4,6-Trimitrobenzene (TATB): Category 1, S, P, F, L. This compound is of considerable interest as a thermally and shock stable explosive for application in warheads of missiles, and in explosive charges for military use or in mining or other civilian uses. A preparation from trichloro-or tribromo-trinitrobenzene is the subject of a patent 1 Kaplan et al (U.S. 3,002,998).

There is no commercial source of this explosive and the starting material, 1,3,5-trichlorobenzene, is not available in the U. S. and must be obtained from West Germany where it is a by-product of pesticide production of Lindane(gamma isomer of hexachlorocyclohexane). Lindane is on EPA's Rebuttable Presumption List of pesticides that may be too dangerous to use.

Production involving the following reactions is being undertaken at NAVORDSTA/IH:

Production of this explosive involves the following supply problems: (1) No domestic source of the final product, intermediate, or starting material; (2) the foreign source of the starting material is a by-product dependent on demand for a major product; and (3) lack of present manufacturing experience and possible scale-up problems. NAVORDSTA, Indian Head, will be making TATB, importing the starting material, 1,3,5-trichlorobenzene. A proposal will be submitted by NSWC, Indian Head, to prepare the starting material, and an investigation will be made for synthetic routes for this material. Trichlorobenzene is a moderately toxic material.

Bis(2,2-Dinitropropyl)-Acetal and Formal: Category 1, P, L, S. These are used in Hi-Frag, MK 73, MK103, MK 107 warheads. These nitroplasticizers were formerly made at the NAVORDSTA/Indian Head and by contractors.

Several years ago, production was discontinued but there is now a resurgence in interest in the use of these materials in certain PBX explosive compositions. Naval Weapons Center has proposed using these nitro-plasticizers in several advance solid propellant formulations and is looking for a source of supply. The previous method of preparation at NAVORDSTA/IH of these compounds involved use of a silver salt. With the increase in the cost of silver and the necessity for removal of silver-containing materials from the process effluents, different synthetic routes will be required. Initial scale-up of new methods of production will be done at the Naval Ordnance Station, and since no supplier is currently available, full-scale production would probably also be done there.

#### Category 2

Caustic Soda and Soda Ash: Category 2, P, L. Caustic soda (sodium hydroxide) has been difficult to obtain because mercury cells are used in its preparation, and there has been a pollution problem of mercury loss from these cells. This compound is used in Tartar motor case reclamation. Soda ash (sodium carbonate) is used in the production of nitrate esters and pH control of waste process water. Much of the production of these compounds is tied up in large contracts for industrial users such as the glass industry. In the past year or so, two major synthetic soda ash plants have shut down: Allied Chemical at Baton Rouge, and Olin at Lake charles. By the end of 1976, Diamond Shamrock plans to close its 800,000 ton-per-year plant at Painesville, Ohio. This will leave only three U. S. synthetic soda ash plants with about two million tons annual capacity: Allied at Syracuse, New York; BASF-Wyandotte at Wyandotte, Michigan and PPG Industries at Corpus Christi, Texas. The implications are that the Navy should let long-term contracts for these materials and keep in close touch with the changing supply situation.

Aluminum Powder: Category 2, E, F, K. Aluminum powder is used in the following programs: Tartar; MK 9, 12, 17, 18 Catapults; 5" Gas Generator; ABL 1362, 1481, 2523, 2912 casting powder; MK 56 Standard Missile; Sidewinder; RAP; MK 103, 107 Warheads; Mk 16 Catapult; and Improved Shrike.

Aluminum powder is purchased under 12 different documents, some of which specify two grades or classes of materials. These various kinds appear to differ principally in particle size range and distribution. An evaluation should be made of whether all of these purchasing documents are really necessary or whether some reduction could be made in documentation and in number of different grades purchased.

Recently, one plant producing aluminum powder was shut down, and there has been difficulty obtaining the spherical Alcoa 120. Since aluminum powder is used in so many programs, any disruption of supply can lead to production problems for the affected Navy programs.

Bauxite, the principal ore for aluminum production, is imported from Jamaica, Surinam, Guyana, and the Dominican Republic. About 84 percent of the U. S. consumption of Bauxite is imported. In the U. S., efforts to demonstrate

that the aluminum industry could survive if overseas supplies of Bauxite were cut off, have concentrated on laterites and clays. Pilot projects using domestic ores can produce aluminum but at a cost about twice that from Bauxite. World Bauxite reserves are expected to last 50 years but the price is expected to go up. As the price increases, processes from clay and other low grade ores will become increasingly competitive.

Aluminum is one of the most energy intensive industrial materials in use.

Perchlorate Salts, Ammonium (AP) and Potassium (KP): Category 2, E, S, K. These two salts are used in a total of 24 programs (18 for AP and 6 for KP). These programs include Tartar, MK 56 Standard Missile, MK 16 Catapult, MK 2 and 3 Gas Generators, MK 103, 107 Warheads, 5" Gas Generator, Sidewinder, etc.for AP; 2.2 KS11,000, MK 16 Catapult, MK 56 Standard Missile, MK 87 Delay Cartridge, MK 18 Cutter, RAP Igniter for KP. Both of these oxidizers are energy intensive, that is, they take a lot of energy for their production. Both are sole source items to Kerr-McGee, and since both are made in the same plant, there may be a problem of plant capacity. It should be noted that AP has eight specifications, and KP three. AP specification WS 12236 is a comprehensive specification; material meeting the requirements of this document is acceptable by any other AP specification. Reducing the number of specifications for these materials would be desirable.

Carbon Black: Category 2, 0, L, K. This material is used in the following: ABL 917, 1362, 1481, 2434 casting powder; the 2.2 KS-11,000; Tartar: MK 80 Shrike Warheads; MK 103, 107 Warheads; Sidewinder; MK 6 Mod 4 Gas Generator: MK 2 and 3 Mod 1 Gas Generators.

Three types of carbon black are produced in the U.S., namely:

- 1. Channel black, from natural gas; only one plant is left in U.S.;
- 2. Furnace black, the major type, which is made from liquid hydrocarbons as the feedstock;
- 3. Thermal black, which uses natural gas but is a batch-type operation.

The supply of carbon black is dependent on the demands of the rubber industry, since it is the major user. The change to smaller cars and the increased use of radial tires are acting to reduce future demand. A cost-price squeeze exists because of the higher cost of the fuels which are all petroleum-based.

There are at least six different specifications used to purchase carbon black. Some of these are poorly written and differences among them are small. It is recommended that these specifications be rewritten and combined into, at most, two or three to expedite location and purchase supplies.

The type carbon black used for ABL 917 casting powder etc., is believed to be channel black which is likely to become unobtainable if the last plant closes.

Tartar, Sidewinder and Shrike are believed to require thermal black which is now made by three producers but which represents only about 7 percent of U. S. production.

Recause of technology changes, cost and availability of raw materials, and changing requirements by the rubber industry which is the principal user, all indications are that DoD requirements may become increasingly difficult to meet.

Graphite: Category 2, F, L, K. Graphite is used in casting powder, Talos, MK 2 Impulse Cartridge, and MK 80 Shrike. The supplier is having difficulty in meeting the specification requirements. In 1973, 100 percent of the U. S. requirement was imported, most of it from Mexico. DoD usage was about six percent of the total. Graphite is one of the materials likely to be in short supply because of a scarcity of both U. S. and world reserves. The problems are likely to involve low DoD total requirement and the fact that four grades, all with different particle size requirements and some with different allowable amounts of moisture, ash, silica and sulfur, are specified. Consideration should be given to whether four different grades are really necessary or whether some could be combined to reduce the purchasing and storage problems involved in handling four different grades of material.

#### Category 3

Viton A: Category 3, S, L. This material is sole source to DuPont Company for use in the Mud Agitator and MK 91 Jato. The company is apt not to bid on requirements if they do not have the material on hand, and they are very independent about supplying the small DoD requirements.

Resins and Plasticizers: Category 3, S, L, K. Most of these are brand name materials, including Epons, Pluracal, Selectrons, Vibrin, P-10 Resin, etc. The problems with these materials are: (1) that they are brand name items, and as such are subject to the manufacturer's changing the process for a different end-item (which may change the properties for our use) or because of an advance in technology or even discontinuing production because of changing markets; (2) the second problem is part of the market response problem, that is, the DoD requirement for these items is very low.

Butarez, Type I & II: Category 3, S, L, K. Phillips Fetroleum is the sole source for this material used in Sidewinder, MK 56 Standard Missile, Mk 9, 12, 17, 18 Catapults, and the 5" Gas Generator. The company is very independent and can force us to take what they offer. Polybutadiene takes nearly 20 percent of the total U. S. butadiene capacity; the lack of new markets is one of butadiene producers' chief concerns.

RDX and HMX: Category 3,E, S, O. RDX (cyclotrimethylenetrinitramine) is used in the MK 73 Warhead, Hi-Frag, and MK 80 Shrike Warhead; HMX (cyclotetramethylenetetranitramine) is used in ABL 2523 and 2912 casting powder, and Trident. Both of these compounds are, (1) sole source, (2) based on petroleum

products, and (3) energy intensive.

The following manufacturing procedures may be used: '

(1) 
$$(CH_2)_6N_4 + 4HNO_3 \longrightarrow (CH_2NNO_2)_3 + 3HCHO + NH_4NO_3$$
  
(hexamethyl- (nitric (RDX) (formal (ammonium ene tetramine) acid) dehyde) nitrate)

(2) 
$$(CH_2)_6N_4 + 2NH_4NO_3 + 5NHO_3 \longrightarrow 2(CH_2NNO_2)_3 + 6H_2O$$
  
(hexamethyl- (ammonium (nitric (RDX) (water) ene tetramine) nitrate) acid)

(3) 3HCHO + 
$$3NH_4NO_3$$
 +  $6(CH_3CO)_2)$   $\longrightarrow$   $(CH_2NNO_2)_{3,4}$  +  $12CH_3COOH$  (parafor- (ammonium (acetic maldehyde) nitrate) anhydride) =3 =4 acid)

Reaction (3) yields MMX (((CH<sub>2</sub>NNO<sub>2</sub>)<sub>4</sub>) and RDX  $\chi$ (CH<sub>2</sub>NNO<sub>2</sub>)<sub>3</sub>) from which HMX can be separated. Several classes of each compound, based on particle size distribution, are purchased.

2-Nitrodiphenylamine: Category 3, S, L. 2-NDPA is used as a propellant stabilizer in double-base propellants, liquid more propellants, mixed plasticizer, Talos, and Terrier. When American Cyananid's plant producing this material blew up, and no other company was action to furnish the material, NAVORDSTA/IH set up and qualified as a source for this material. American Cyanamid started manufacture of 2-NDPA on a limited cole after rebuilding but NAVORDSTA/IH is still qualified as a second source.

Desensitizing Wax: Category 3, S, L, O. This material is used in compositions D-2 and A-3 and in the Explosive H-6. Only one supplier is available and at times supplies are uncertain. Because of this problem, new sources of waxes are under investigation. The NAVSURWPNSCTR and NAVWPNSTR have been studying the wax replacement problem. They have looked at waxes from non-petroleum sources such as Douglas fir bark, wheat and tallow derivative, aqueous lattices (Latexes), Airflex 400, 401; 401 from Air Products, and Ultrathene VE 638X from USI Chemicals. The VE 638X, which is an ethylene acetate copolymer, appears to be a suitable substitute for the D-2 wax used in the preparation of A-3. Further in the future, research on the application of the oily wax from the seeds of the Jojoba plant may turn up another possible substitute.

Ammonium Ferri-Ferrocyanide Complex (Milori Blue): Category 3, S, K, L. This material is used in the Tartar and MK 2 and 3 Mod 1 Gas

Generators. When the former supplier went out of business, there was difficulty finding and qualifying a new supplier. Currently, only one company is qualified to provide acceptable material. Total DoD consumption is small, and the supply situation for this substance should be watched.

#### Category 4:

Lead Salts: Category 4, P. Because of pollution problems related to lead compounds, the increasing dispersion in the environment and the fact that some lead compounds are suspected carcinogens, industrial uses of these compounds present problems. The following lead compounds are used in ordnance production at NAVORDSTA, Indian Head.

Compound	Use
Dextrinated Lead Azide	Mk 136 Delay Cartridge, MK 18 Cartridge Actuated Cutter
Lead Beta Resorcylate	ABL 917, 1362, 1481 Casting Powder
Lead Chromate	MK 9, 12, 17, 18 Catapults, CADs
Lead Dioxide	MK 17 Ignition Element
Lead 2-Ethyl Hexoate	ABL 705 Casting Powder
Lead Nitrate	MK 16 Mod O Catapult
Lead Oxide (Pb <sub>3</sub> 0 <sub>4</sub> )	ABL 1525, 40-pound charge
Lead Salicylate	ABL 705, 917, 1362, 1481 Casting Powder
Lead Styphnate	MK 82 Impulse Cartridge, MK 80 Shrike Warhead, CAD Igniters
Tribasic Lead Maleate Mono- hydrate (Trimal)	ABL 2434 Casting Powder

Lead chromate is a recognized carcinogen and lead oxide ( $Pb_3O_4$ ) is a suspected carcinogen. Lead is a cumulative poison. The toxicity of the various lead compounds appears to depend on several factors:

- (1) Solubility of the compound in the body fluids
- (2) Fineness of the particles
- (3) Conditions of use, e.g., dust hazard with dry powders

The carbonate, monoxide and sulfate are considered to be more toxic than metallic lead or other lead compounds.

Adequate reserves of lead exist in the U. S. and any supply problems are likely to be due to EPA and OSHA requirements or controls, and possible spot shortages of such compounds as the resorcylate, 2-ethyl hexoate, and salicyate which are made primarily for the commercial market and for which the DoD total requirements are quite small. The primary explosives lead azide and lead styphnate are currently being supplied by Olin. It is believed that supplies of these will continue to be furnished by contractors operating their own or government-owned plants.

Trichloroethylene: Category 4, P. Trichloroethylene is used in Tartar and is widely used as a solvent. It is quite toxic by inhalation and fatalities have been observed after severe acute exposure. In the last few months, several reports have indicated that it may be carcinogenic and OSHA/EPA action to control or forbid its usage is probable.

2,4-Toluene Diisocyanate (TDI): Category 4, P, O, K. This compound is used in Tartar, MK 56 Standard Missile, MK 73 Warhead, Hi-Frag, MK 103, 107 Warheads, Forty-pound Charge, and MK 80 Shrike Warhead. TDI is extremely toxic with a threshold limit value of 0.02 parts per million or 0.1% mg/m³. For comparison, the values of hydrogen cyanide are 10 and 11, respectively. Because of this high toxicity, it is possible that OSHA/EPA requirements may be put into effect to control use and exposure.

This compound is made from toluene and hence is petroleum based. It is purchased according to five applicable documents, some of which refer to two types or grades. It would be desirable to review these documents and combine them into one or two specifications.

Pentachlorophenol: Category 4, P. This substance is used as a wood preservative for treatment of the shipping crates of Zuni and other Navy missiles. Pentachlorophenol, along with creosote(another wood preservative), and about 40 herbicides, fungicides and insecticides, are on a list issued by EPA of substances that may be too hazardous to man or the environment to allow continued use. Pentachlorophenol has a high toxicity by ingestion, inhalation and skin absorption, and chronic exposure can cause liver and kidney damage.

Phenyl Beta-Naphthylamine: Category 4, P. This material, also known as Neozone U, is used in Tartar, MK 56 Standard Missile, MK 73 Warhead, and Hi-Frag. Details of the toxicity of the phenyl derivative are unknown. The phenyl compound is made by reaction of aniline and beta-naphthol and not via the carcinogenic beta-naphthylamine. The situation should be watched in case the phenyl derivative turns out to have highly toxic or carcinogenic properties. Beta-naphthylamine is on the OSHA list as a known carcinogen causing bladder cancer.

Shelldyne-H: Category 4, P. Norbornadiene is a starting material for Shelldyne-H, a fuel for Navy cruise missiles. This substance (norbornadiene) is a by-product of Shell's insecticide production which the government considers a health hazard. The Shelldyne-H is an isomeric mixture of three hydrogenated dimers of norbornadiene, exo-endo hexacyclic isomer - 20% by volume, endo-endo hexacyclic isomer - 70% by volume, exo-trans-exo pentacyclic isomer - 10% by volume. Restriction of insecticide production and thus of norbornadiene, could have an adverse effect on production of this missile fuel.

Kevlar: Category 4, P. Kevlar is a high-strength fibrous aramid resin introduced by DuPont in 1974; it exhibits high performance properties obtainable through specific polymer molecular chain orientation. It's proposed uses extend from bulletproof vests to nozzle throats in high altitude rockets to nose cone ablatives on atmospheric re-entry vehicles.

Commercial production of Kevlar, however, may be delayed a year or more as a result of DuPont's laboratory tests showing the solvent, hexamethylphosphoramide (HMPA), to be cancerous to rats. After eight months of inhaling varying amounts of HMPA, most of the rats developed nasal tumors that often spread to the brain even at doses as low as 40 parts per billion. These tests do not mean that HMPA would have the same effect on humans but production of Kevlar has ceased until a new solvent has been found.

#### Category 5

Barium Chromate, Ammonium Dichromate, and Chromium: Category 5, P, F. Barium chromate is used in the MK 56 Standard Missile, MK 9, 12, 17, 18 Catapults, and CADs; ammonium dichromate is used in the MK 2 and 3 Mod 1 Gas Generators. Supply problems are likely to be related to EPA or OSHA requirements, since chromate salts are recognized carcinogens of the lungs and nasal cavity, and also experimental carcinogens of the stomach and larynx. Also, chromium is a critical material since 100 percent of the U.S. consumption is imported, principally from the Soviet Union, South Africa, Turkey and the Phillipines. DoD usage amounts to six percent of the U.S. consumption. Chromium and chromium salts are likely to be in short supply because of the scarcity of U.S. reserves and politicoeconomic factors affecting world trade.

The supply situation for chromium and chromium-containing materials is one of the most critical, since the world reserves are in potentially hostile areas, such as the Soviet Union, or in countries which are subject to political instability or from which the supply routes are very long. For many uses of chromium and its salts, there do not appear to be viable alternatives. However, the following alternate materials for chromium have been suggested:

Present Use	Alternate Material		
Stainless steels containing chromium	Titanium-carbon steels, aluminum, enameled or painted steels		
Chromium pinte	Nickel, zinc, enamel, plastics		
Chrome yellow (lead chromate or barium chromate)	Cadmium yellow		
Chromite	Magnesite		

Some planners have suggested that ornamental uses of chromium, such as automibile trim, etc., be banned, so that the chromium supply could be conserved for industrial and other uses where no feasible substitute exists.

Manganese Powder and Manganese Delay Composition: Category 5, F. These materials are used in CADs and the MK 9, 12, 17, 18 Catapults. Manganese and its compounds should be regarded as critical materials since 84 percent of the U. S. consumption is imported, principally from Gabon, Brazil, South Africa and Zaire. All of these sources have long overseas supply routes and all may be subject to political instability with resultant economic and transport problems.

Titanium Dioxide and Titanium: Category 5, F. Titanium dioxide (rutile crystal) is used in the MK 9, 12, 17, 18 Catapults, MK 56 Standard Missile, and 5" Gas Generator. Titanium powder is used in the MK 17 Ignition Element.

The intire U. S. consumption of rutile (TiO2) is imported, essentially all r it from Australia. About 32 percent of the other important titanium ore, ilmenite, is imported with most of it coming from Canada and a lesser amount from Australia. In 1974, 25 percent of the U. S. requirements for unrefined titanium metal (sponge) was imported from Japan and the Soviet Union. Aircraft and space applications utilize about 90 percent of the current production of the metal. Titanium dioxide is an important pigment.

Tungsten Powder: Category 5, F, K. Tungsten (now called Wolfram) is used in the MK 87 Delay Cartridge and the RAP Igniter. Tungsten is one of the elements for which imports comprise more than 50 percent of U. S. consumption. The principal sources for imports are Canada, Peru, Australia and Mexico. Tungsten is in the natural stockpile. Major uses are ferroalloys, carbides, lamp filaments, electronics. DoD usage, which includes such applications as the throat in solid-fuel rocket engine nozzles, is seven percent of U. S. consumption. For delay cartridges and igniters, both purity (greater than 99.1%) and the nature of impurities are critical. Maximum

values are specified for 13 elements, ranging from 0.001% tin to 0.03% for molybdenum.

Glyceryl Mono-and Tri-ricinoleates: Category 5, S, F. These esters are found in castor oil and are both used in Tartar and the MK 56 Standard Missile. They are sole source items, and since more than 50 percent of the castor oil is imported, chiefly from Brazil and India, there is dependence on overseas sources.

Cobalt Naphthenate: Category 5, F, L. This compound, the cobalt salt of hexahydrobenzoic acid, is used in Asroc, 2.2KS11,000, MK16 Mod 0 Catapult, MK 73 Warhead, SGU. Cobalt and its salts are critical materials because practically the entire U. S. consumption of cobalt must be imported, principally from Zaire. DoD usage of cobalt is 13 percent of U. S. consumption. The amount of this compound used in ordnance materials is small and production is geared to the commercial market.

Shellac: Category 5, F. Shellac is used in electronic equipment as water-proofing and as an insulator, and in pyrotechnic compositions for the same purposes. The U. S. is dependent on imports for more than 50 percent of its annual consumption with Thailand and India the major sources of supply. Picatinny Arsenal has done some work on finding a substitute for shellac in Pettman cement and similar water-proofing applications. They found that a mixture of rosin and ethyl cellulose could be substituted for shellac when the proportions of other ingredients in the compositions are modified. If it appears that the supply situation is likely to deteriorate, consideration should be given to stockpiling or wider use of substitute materials wherever possible.

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Elba Solvent: Category 5, F.This is a mixture of ethyl lactate and butyl acetate used in Asroc. Rapec, MK 66, Zuni, Chaffroc, MK 91 Jato. The supplier has reduced the amounts available and it may be necessary to find a foreign source. A supply from the domestic reserve is still available but the future outlook is uncertain.

Nitroform: Category 5, F, L. This compound is used in the preparation of TEFO and FEFO for propellants at the Naval Ordnance Station, Indian Head, Md. Present supplies were made in Sweden by reaction of acetylene with nitric acid. It was formerly made at the Naval Ordnance Station by a different process. Supply problems are believed due to lack of a commercial market and small requirements.

Ammonium Oxalate: Category 5, F, L. This compound is used in the MK 6 Mod 4 Gas Generator. DoD usage is small and in the recent past, there was no U. S. producer and the compound was in short supply. It is possible that shortages may recur.

Sodium Barbiturate: Category 5, F, L. This compound is used in the MK 6 Mod 4 Gas Generator. In 1974, this compound was in short supply and there was no U. S. producer. Annual DoD usage is small and there may be supply problems in the future.

#### Category 6:

Zirconium, Zirconium-Nickel Alloy and Zirconium Oxide: Category 6, K, S. Zirconium powder is used in thermal batteries, CADs, MK 9, 12, 17, 18 Catapults; Zirconium-nickel alloy and zirconium oxide are used in the MK 18 Cartridge Actuated Cutter.

Zirconium metal powder is usually made by one of two processes. One is by reduction of the oxide, while the other is the decomposition or pyrolysis of the halide (usually chloride or iodide) salt, at about 1200°C, to give depositions of very pure zirconium sponge.

The biggest problem has been in procurement of zirconium powder for use in rapid-rise-time thermal batteries. There is only one commercial plant (Ventron Corporation) left in the U. S. making zirconium powder; the other (Foote-Mineral) discontinued manufacture after their facility for zirconium burned down. Ventron Corporation has a limited production capacity and has been unable to meet specifications for the zirconium.

A Tri-Service Ad Hoc Committee has been set up to look into this problem. The NAVORDSTA, Indian Head, has submitted a proposal for a timely establishment of a production process which will provide the DoD with an assured technology for zirconium powder production in case no commercial vendor is available.

Ferric Oxide: Category 6, K. This compound is used in the Tartar, MK 56 Standard Missile, MK 9, 12, 17, 18 Catapults, 5" Gas Generator and CADs.

There has been a problem with particle size and purity. Some of the material received does not meet the specification which requires 99.4 percent purity as  $Fe_2O_3$  for use in Tartar and MK 56. For the other applications, two types and three classes are specified, the differences being in purity and particle size distribution.

#### SUMMARY

A survey has been made to evaluate the criteria which determine whether a substance, required for the production of propellant and related Navy materials, is critical, and for which materials alternate sources are required or should be developed. Six categories of materials have been examined:

(1) Materials not commercially available or unavailable in the

grades and quantities required. These include 1,1-dimethylhydrazine (UDMH); 2,4-dinitrophenoxyethanol; 2,4-toluene-diamine; tris(2-methyl-1-aziridinyl) phosphine oxide (MAPO); nitroguanidine; nitrocellulose; bis(2,2-dinitropropyl)-acetal and formal; 1,3,4-triamino-2,4,6-trinitrobenzene (TATB). Most of these materials are currently being manufactured or processed at the Naval Ordnance Station, Indian Head, Maryland.

- (2) Materials commercially available but which present supply problems for a variety of reasons. These include sodium hydroxide (caustic soda) and sodium carbonate (soda ash), aluminum powder, ammonium and potassium perchlorate, carbon black and graphite.
- (3) Materials which are sole source; these include proprietary polymers and resins as well as other materials. Examples are, Viton A, Butarez, resins and plasticizers such as Epons and Selectrons, 2-nitrodiphenylamine, desensitizing wax, Milori Blue, REX and HMX.
- (4) Materials for which a starting material, process, intermediate, or final product may involve medical/OSHA/EPA problems; examples are, lead salts, trichlorethylene, 2,4-toluene disocyanate (TDI), pentachlorophenol, phenyl-beta naphthylamine, Shelldyne-H and Kevlar.
- (5) Materials primarily dependent on foreign imports; among these are chromium and its salts, manganese and its compounds, titanium and its salts, tungsten, castor oil derivatives, cobalt and its salts, shellac, Elba solvent, nitroform; ammonium oxalate and sodium barbiturate.
- (6) Materials with specification problems; these include zirconium, zirconium oxide and ferric oxide.

Many of the above materials fall into more than one category and the classification is simply a grouping of substances with similar characteristics in the supply system.

#### **CONCLUSIONS**

Some of the reasons found for materials being on a critical list are the following:

- (1) Sole source: Because of varying reasons, a sole source supply is required; reasons may include; only manufacturer available, certain specific physical or chemical properties, etc.
- (2) Quantity requirements are low: The material may only be ordered infrequently, albeit in large quantities, and companies do not want to stock excess.

- (3) DoD often exceeds 90 percent of usage: Many materials are required only by DoD or else DoD is the main buyer; companies would rather have a large commercial market.
- (4) Poor visibility in chain of use: Some materials come in short supply 'all of a sudden' when in reality, the shortage is seen in other areas but the connection is not made because of layers of contracts from raw ingredient to final use; examples are solvents used in making dyes and in making Kevlar.
- (5) New OSHA, EPA requirements: A prime example is the closing of FMC's plant which manufactured UDMH; OSHA regulations against the use of nitrosoamines, one of which FMC used in the manufacture of UDMH, a rocket fuel used by the Air Force, caused a shortage of UDMH during 1974 and 1975. More examples where OSHA or EPA edicts may cause a critical shortage are in the use of trichloroethylene and in OSHA's proposed standard #45933 in the Federal Register, Vol. 40, No. 193 of 3 October 1975, on occupational exposure to lead and lead compounds.
- (6) No substitution: When an ingredient is seen to be in short supply, or heading that way, it is difficult and time-consuming often in terms of years and millions of dollars-to obtain exceptions to specifications in order to substitute another more plentiful and sometimes superior material because of requalification problems.
- (7) Technical growth or obsolescence: Many materials become hard to get or disappear from the market; for example, being a by-product of a process, they are no longer available when the state-of-the-art advances and better processes are found and utilized which have different by-products; a second example is of changing markets due to technology advances where the public no longer desires the product, so the company changes to a different product.

#### FUTURE PLANS

Work will continue on completion of a comprehensive list of propellant and explosive ingredients used by NAVSEA in current and planned projects. A laboratory phase of the program will seek acceptable substitutes and describe methods for their utilization. In conjunction with the substitute routes, efforts will be made during FY 77 to initiate ways of improving and shortening the time needed to obtain exceptions to specifications.

Materials which will be examined to determine if the usual or an alternate process might be feasible for local production include: Elba solvent (esterification of lactic acid to produce the ethyl lactate), Milori Blue (production of the ammonium ferri-ferrocyanide complex), ammonium oxalate, and sodium barbiturate.

Materials for which substitutes will be sought include: Pentachlorophenol, phenyl-beta-naphthylamine, TDI, resins and plasticizers, shellac, and castor oil esters.

Materials for which the specifications will be examined to see if the number and variety could be reduced include: Aluminum, ammonium perchlorate, carbon black, and graphite.

#### **BIBLIOGRAPHY**

Since much of the information was obtained from interviews with chemists and engineers at the Naval Ordnance Station, Indian Head, and other informed sources, detailed references are not being included in this report. Major written sources include but are not limited to the following:

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- 7. The Wall Street Journal, 1974 June 1976.

Table I

U. S. DEPENDENCE ON IMPORTS OF PRINCIPAL INDUSTRIAL RAW MATERIALS WITH PROJECTIONS TO 2000 1

Raw Material	1950	1970	1985	2000
Aluminum	64	85	96	98
Chromium	N/A	100	100	100
Copper	31	0	34	56
Iron	8	30	55	67
Lead	39	31	62	67
Manganese	88	95	100	100
Nickel	94	90	<b>88</b> .	89
Phosphorus	8	0-	0	2
Potassium	14	42	47	61
Sul fur	2	0	28	52
Tin	77	N/A	100	100
Tungsten	N/A	50	87	97
Zinc	38	59	72	84

<sup>1</sup> THE FUTURIST, June 1975, p. 131.

# Table II CRITICAL MATERIALS\* DEPENDENT ON FOREIGN SOURCES

Chromium: 100% dependent; sources are Rhodesia, U.S.S.R., South Africa

Niobium (Columbium): 100% dependent; sources are Brazil, Malaysia, Záfre

Platinum metal: Platinum/palladium as catalysts; 100% dependent; sources

are U.S.S.R., South Africa, Canada

Natural Rubber: 100% dependent; source is Southeast Asia

Castor Oil: Greater than 50% dependent

Shellac: Greater than 50% dependent

Cobalt: 100% dependent; sources are Zaire, Belgium, Norway, Canada

Tin: 100% dependent; sources are Malaysia, Thailand

Nickel: Approximately 90% dependent; sources are Canada, Norway

Manganese: Approximately 85% dependent; sources are Gabon, Brazil, Rep.

of South Africa, Zaire

Mica: 100% dependent; sources are India, Brazil, Malagasy Republic

<sup>\*</sup> Materials used at NAVORDSTA, Indian Head, Md.

Table III
WORLD MARKET, EXPORTABLE MINERALS

Copper: Most of world's supply exported from Chile, Peru, Zambia, Zaire

Tin: 70% of all tin exported from Malaysia, Bolivia, Thailand

Lead: 60% of all lead comes from Australia, Mexico, Peru

Nickel: Over 50% of world reserves are in Cuba, New Caledonia

Cobalt: Known reserves are in Zaire, Cuba, New Caledonia

Table IV
ENERGY INTENSIVE INDUSTRIES

Industry	Percent of U.S. Energy Expenditure
Iron and Steel	5.4
Petroleum Refining	4.4
Paper	2.0
Petrochemical Feedstocks	2.0
Aluminum	1.1
Copper	0.8

# SUPPLEMENTARY

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## NAVAL SURFACE WEAPONS CENTER WHITE OAK LABORATORY





To all holders of NSWC/WOL/MP 76-19

Title:

Alternate Sources for Propellant Ingredients

Change 1

Approved by Commander, NAVSURFWPNCEN

E. McQUISTION

15 page(s)

By direction

This publication is changed as follows:

#### 2-Nitrodiphenylamine

Change lines 5 to 7 of this paragraph to read as follows:

NAVORDSTA/IH did preliminary manufacture to qualify as a second source. American Cyanamid has been supplying 2NDPA from a reserve stock, and NAVORDSTA/IH is hoping to become qualified as a second source.

Insert this change sheet between the cover and the DD Form 1473 in your copy. Write on the cover "Change 1 inserted"